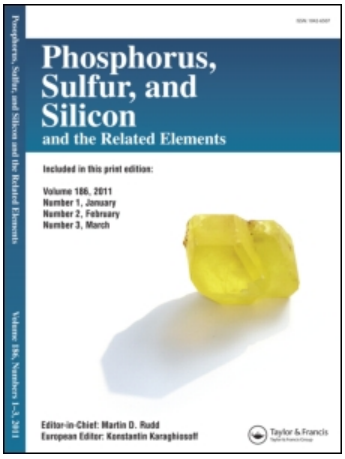
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIONS OF O-(ALKYLCHLOROFORMOIMINO)-TRICHLOROMETHYLPHOSPHORANES WITH S-NUCLEOPHILES

Yu. E. Lyashenko[a]; V. B. Sokolov[a]
[a] Institute of the Physiological Active Substances of the USSR Academy of Sciences, Moscow region, USSR

To cite this Article Lyashenko, Yu. E. and Sokolov, V. B.(1992) 'REACTIONS OF O-(ALKYLCHLOROFORMOIMINO)-TRICHLOROMETHYLPHOSPHORANES WITH S-NUCLEOPHILES', Phosphorus, Sulfur, and Silicon and the Related Elements, 69: 1, 153 — 161
To link to this Article: DOI: 10.1080/10426509208036864
URL: http://dx.doi.org/10.1080/10426509208036864

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1992, Vol. 69, pp. 153–161
Reprints available directly from the publisher
Photocopying permitted by license only

© 1992 Gordon and Breach Science Publishers S.A.
Printed in the United Kingdom

REACTIONS OF O-(ALKYLCHLOROFORMOIMINO)-TRICHLOROMETHYLPHOSPHORANES WITH S-NUCLEOPHILES

YU. E. LYASHENKO and V. B. SOKOLOV

Institute of the Physiological Active Substances of the USSR Academy of Sciences, Chernogolovka, Moscow region 142432, USSR

(Received September 13, 1991; in final form January 6, 1992)

Interactions of O-(alkylchloroformoimino)trichloromethylphosphoranes with hydrogen sulfide and mercaptans are reported; interaction with 2-mercaptoethanol is discussed and activation of the chlorine at a sp^2 hybridized carbon by means of the phosphorane fragment is demonstrated in the substitution reactions with S-nucleophiles; the method of P=S bond formation in chlorophosphoranes by means of the reaction with thioacetic acid is suggested; some derivatives of O-alkylchloroformooximes are described.

Key words: O-(alkylchloroformoimino)trichloromethylphosphoranes; O-(alkylchloroformoimino)chloromethylthionophosphonates; O-(alkylchloroformoimino)-O-alkylmethylthionophosphonates; bis(O-methylchloroformoimino)methylphosphonate; O-[methyl-S-(β-chloroethyl)formoimino]chloromethylphosphonate; O-(methyl-S-acetylformoimino)chloromethylthionophosphonate.

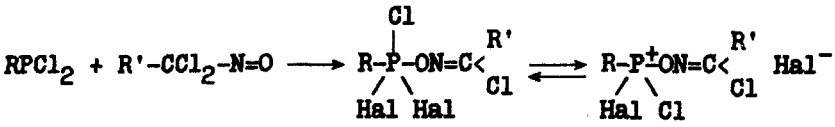
Downloaded At: 14:44 29 January 2011

INTRODUCTION

Recently we described the preparation and some properties of the oxochlorophosphoranes **1** with a

$$-O-N=C<^{Alk}_{Cl}$$

ligand[1]:



$$RPCl_2 + R'-CCl_2-N=O \longrightarrow R-P(Hal)(Hal)-ON=C<^{R'}_{Cl} \rightleftharpoons R-P^{\pm}(Hal)(Cl)-ON=C<^{R'}_{Cl}\ Hal^-$$

1 (1)

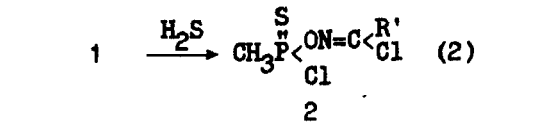
CH_3PCl_2, $C_6H_5PCl_2$, $ClCH_2PCl_2$, $BrCH_2PBr_2$, $(CH_3)_2C=CHPCl_2$

R'= CH_3, C_2H_5, C_3H_7, i-C_3H_7, C_4H_9, CH_2Cl

In this report the reactions of O-(alkylchloroformoimino)trichloromethylphosphoranes **1** with various S-nucleophiles (hydrogen sulfide, mercaptans, 2-mercaptoethanol, mercaptoacetic acid, thioacetic acid) are discussed.

RESULTS AND DISCUSSION

The chlorides of O-(alkylchloroformoimino)methylthionophosphonic acids **2** (Tables I and II) were obtained by the reaction of **1** with hydrogen sulfide [Equation (2)]:



R'= CH_3, C_2H_5, C_3H_7, i-C_3H_7, C_4H_9, CH_2Cl

TABLE I

Physical properties of O-(alkylchloroformoimino)chloromethylthionophosphonates **2**

No.	Compound[a]	Yield[b] (%)	B.p. (°C/mm Hg)	n_d^{20}
2a	$CH_3P(S)(Cl)ON=CClCH_3$	35;56[c]	60-62/3	1.5380
2b	$CH_3P(S)(Cl)ON=CClC_2H_5$	30	95/3	1.5278
2c	$CH_3P(S)(Cl)ON=CClC_3H_7$	27;64[c]	96-100/3	1.5222
2d	$CH_3P(S)(Cl)ON=CClC_3H_7$-i	21;54[c]	86/3	1.5140
2e	$CH_3P(S)(Cl)ON=CClC_4H_9$	24	98/3	1.5170
2f	$CH_3P(S)(Cl)ON=CClCH_2Cl$	33	101/3	1.5454

[a]Satisfactory microanalyses obtained: C±0.5 H±0.5 N±0.5
[b]Yield of isolated product (when hydrogen sulfide was used)
[c]Yield of isolated product (when thioacetic acid was used)

TABLE II

NMR spectroscopic data of O-(alkylchloroformoimino)chloromethylthionophosphonates **2**

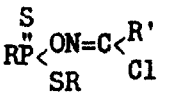
No.	^{31}P-NMR (ppm)	^{1}H-NMR ($CDCl_3$/TMS, δ, ppm)
2a[1]	100.6	2.45s 3H;2.46d 3H 15Hz
2b[1]	100.8	1.32t 3H 8Hz;2.40d 3H 15Hz;2.73m 2H 8Hz
2c[1]	100.5	0.99t 3H 7Hz;1.79m 2H;2.44d 3H 14Hz;2.66t 2H 7Hz
2d[1]	100.7	1.28d 6H 7Hz;2.43d 3H 14Hz;3.0m H 7Hz
2e[1]	100.5	0.95t 3H 7Hz;1.40m 2H;1.71m 2H; 2.46d 3H 15Hz; 2.66t 2H 7Hz
2f[1]	101.3	2.47d 3H 15Hz;4.45s 2H

[1]IR-spectrum, ν, cm^{-1}: 1600 (C=N)

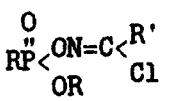
It is known that mercaptans also can be used for the formation of a thiophosphoryl group P=S in chlorophosphoranes.[2-5] However in the case of O-(alkylchloroformoimino)trichloromethylphosphoranes the reaction with mercaptans mainly proceeds with the formation of an energetically advantageous phosphoryl group P=O

Downloaded At: 14:44 29 January 2011

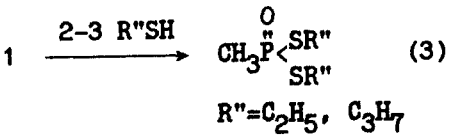
through decomposition of an alkylchloroformoiminoic fragment. Dithioalkylphosphonates were the main products isolated from a reaction mixture when 2–3 moles of mercaptan to one mole of phosphorane were added. Attempts to obtain esters



similar to

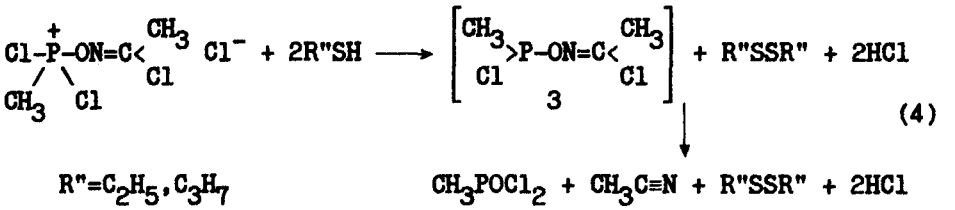


(Reference 1) were unsuccessful:



(3)

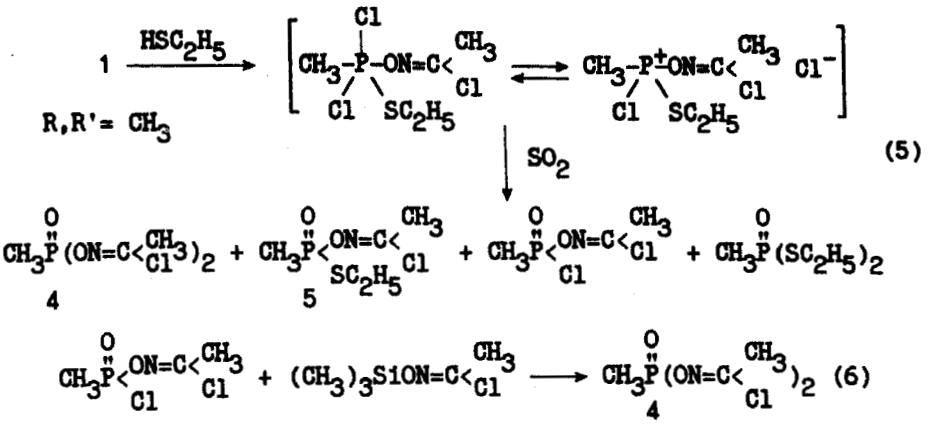
Formation in large quantity of methylphosphonic acid dichloride and a corresponding disulphide probably is due to the reduction of a phosphonium isomer[5] and the subsequent decomposition of **3**[1]:



(4)

Additional stabilization of the ionic form of phosphorane **1** is achieved, when a chlorine at phosphorus is substituted by the less electronegative thioalkyl group. This shifts the equilibrium in Equation (5) to the phosphonium isomer and makes possible the intermolecular exchange of ligands resulting in the formation of bis(O-methylchloroformoimino)methylphosphonate **4**. Also **4** was obtained when O-(methylchloroformoimino)trichloromethylphosphorane was treated with moist C_3H_7SH. The structure of **4** was proved with an independent synthesis [Equation (6)] in addition to physicochemical methods. Owing to the fact that the reaction with thiols proceeds in several directions the yield of O-(methylchloroformoimino)-S-ethylmethylthiophosphonate **5** is extremely low (2–3%). **5** was identified by ^{31}P-NMR in comparison with an authentic sample):

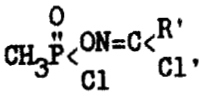
Downloaded At: 14:44 29 January 2011



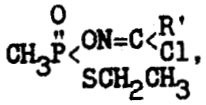
(5)

(6)

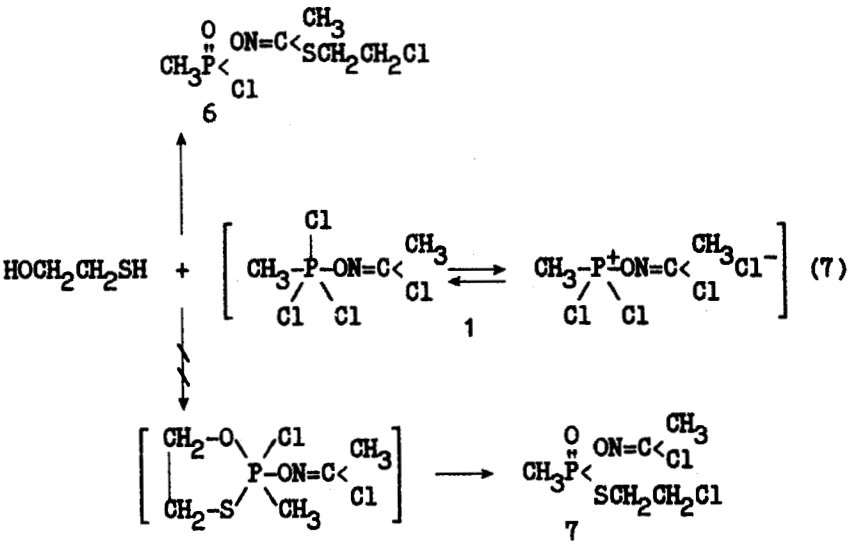
In the reaction with 2-mercaptoethanol [Equation (7)] O-[methyl-S-(β-chloroethyl)formoimino]chloromethylphosphonate **6** was obtained instead of the expected S-(β-chloroethyl)-O-(methylchloroformoimino)methylthiophosphonate **7**. The structure of **6** is confirmed by the typical ^{31}P-NMR value (about 44 ppm for



about 62 ppm for

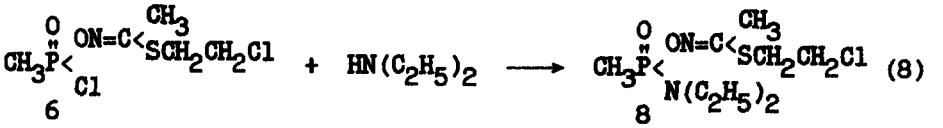


References 6 and 7) and with the synthesis [Equation (8)] of N,N-diethylamido-O-[methyl-S-(β-chloroethyl)formoimino]methylphosphonate **8**. The reaction [Equation (7)] is sensitive to steric factors. When R′ = C_3H_7, i—C_3H_7 the reaction [Equation (7)] ends with the formation of an unseparable mixture of products.



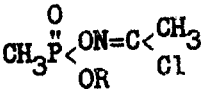
(7)

Downloaded At: 14:44 29 January 2011

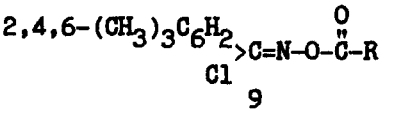


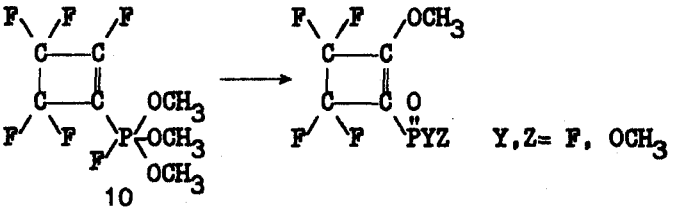
The formation of the chloride **6** is to be expected when taking Pearson's concept of HSAB into account. The principle of affinity of hard acids to hard bases is clearly illustrated by the difference in the reaction ability of a chlorine at a phosphorus in **1** with respect to OH— and SH— groups. Phosphoranes **1** and alcohols interact at a temperature below $-50°C$,[1] but it is observed that the substitution of a chlorine at phosphorus in **1** with a thioalkyl group begins at a temperature above $-7°C$ and becomes essential at a temperature about $+2°C$. According to Reference 8 the "carbon basicity" of a thiol anion is 10^4 times as much as the same of a corresponding oxide anion.

It is necessary to note that the chlorine in model compounds



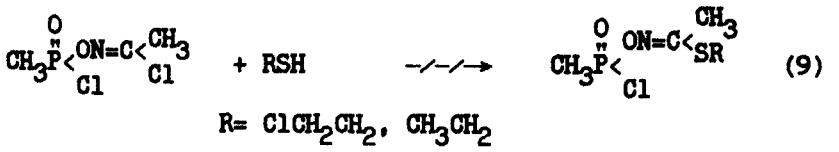
demonstrates high inertness in substitution reactions. O-(Methylchloroformoimino)-O-alkylmethylphosphonates do not react with alcohols and the reaction proceeds with splitting off of the methylchloroformoiminoyl group when alcoholate is used. The unreactivity of a chlorine in the similar structure **9** was reported.[9] On the other hand the substitution of the vinylic fluorine during decomposition of the phosphorane **10** occurs and the authors report that the $—P(O)(OCH_3)_2$ group activates the vinylic halogen.[10]





In our case the absence of the interaction of O-(methylchloroformoimino)chloromethylphosphonate and β-chloroethanethiol rule out the possibility of the activating influence of the phosphoryl group [Equation (9)]. Ethanethiol, from which a greater activity was to be expected, also did not react with O-(methylchloroformoimino)chloromethylphosphonate [Equation (9)]:

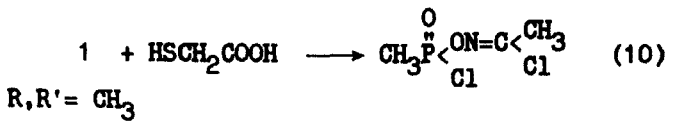
Downloaded At: 14:44 29 January 2011



(9)

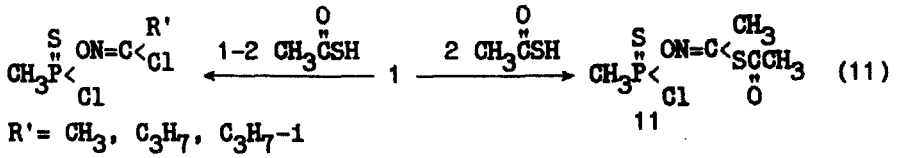
It is known that substituents with a strong electronegative effect promote a nucleophilic substitution at a sp^2 hybridized carbon in olefinic and aromatic compounds. Evidently in the reaction according to Equation (7) a chlorophosphonium cation $Cl_2\overset{+}{P}\langle$ which is a strong acceptor[5] promotes a nucleophilic substitution at a sp^2 hybridized carbon in **1** and then a phosphoryl group P=O is formed.

Probably the extreme facile formation of the phosphoryl group P=O from **1** and a carboxyl group[1] makes impossible a substitution in methylchloroformoimino group in the reaction [Equation (10)] with mercaptoacetic acid:



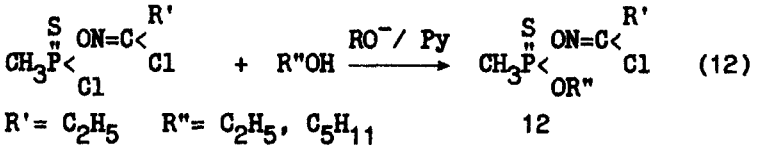
(10)

Supposing the cause of the formoiminogroup decomposition in the reaction with thiols [Equation (2)] is the difficulty of breaking off of S—$C_{aliphatic}$ bond we used thioacetic acid for P=S bond formation and obtained O-(alkylchloroformoimino)chloromethylthionophosphonates **2** with increased yields (Tables I and II). When R' = CH_3 the product **11** was obtained when 2 moles of thioacetic acid were added:



(11)

O-(Alkylchloroformoimino)chloromethylthionophosphonates **2** obtained according to Equations (2) and (11) can be converted to O-(alkylchloroformoimino)-O-alkylmethylthionophosphonates **12** by the typical reactions [Equation (12)]:



(12)

Also reactions of hydrogen sulfide and thioacetic acid with O-(alkylchloroformoimino)trichlorophenylphosphoranes were studied. As a rule in this case the reactions become complicated by the side reactions of O-(alkylchloroformoimino)trichlorophenylphosphoranes[1] which result in the formation of a mixture of products.

Downloaded At: 14:44 29 January 2011

EXPERIMENTAL

^{1}H-NMR and ^{31}P-NMR (Reference 85% H_3PO_4 ext, negative chemical shifts are upfield of the standard) spectra were recorded on a Bruker CXP-200 spectrometer, IR spectra were recorded on a Specord IR-75 spectrometer. Phosphoranes[1] and β-chloroethanethiol[11] were prepared according to the literature. Experiments were conducted with careful exclusion of moisture.

Interaction of O-(alkylchloroformoimino)trichloromethylphosphoranes with hydrogen sulfide (**2**), *General Procedure:* A solution of O-(alkylchloroformoimino)trichloromethylphosphorane (50 mmol) in toluene (50 ml) was stirred at 0– + 10°C while H_2S (60 mmol) was added. Toluene was removed under vacuum. The residue was fractionated and the corresponding O-(alkylchloroformoimino)chloromethylthionophosphonate **2** was obtained (Tables I and II).

Interaction of O-(methylchloroformoimino)trichloromethylphosphorane with ethanethiol (**3**): A solution of O-(methylchloroformoimino)trichloromethylphosphorane (81 mmol) in toluene (170 ml) was stirred at −5– + 5°C while ethanethiol (15.3 g, 240 mmol) was added. The mixture was allowed to warm to room temperature and then was kept at 80°C during 0.5 hour. Toluene was removed under vacuum and the residue was distilled to give S,S-diethylmethyldithiophosphonate (4.7 g, 25 mmol, 31%) with b.p. 100–103°C/3 mm Hg, n_d^{20} 1.5816. ^{31}P-NMR 77.7 ppm. ^{1}H-NMR spectrum, δ: 1.4t 6H J8; 2.22d 3H J 14; 2.92m 4H J8. Also ethyl disulphide was obtained, b.p. 150°C/760 mm Hg, n_d^{20} 1.500, ^{1}H-NMR, δ: 1.3t 3H J7.5; 2.65m 2H J7.5. A similar result was obtained with C_3H_7SH.

Interaction of O-(methylchloroformoimino)trichloromethylphosphorane with ethanethiol and sulphur dioxide (**5**): A solution of O-methylchloroformoimino)trichloromethylphosphorane (44 mmol) in toluene (80 ml) was stirred at −2.5– + 1.5°C while ethanethiol (2.7 g, 43 mmol) was added. The mixture was stirred at 0°C for 10 minutes and at −20°C for 20 minutes and then SO_2 (6.2 g, 97 mmol) at −20– −30°C was added. The mixture was stirred at −10– −15°C for 30 minutes and then allowed to warm to room temperature. Toluene was removed under vacuum and the residue was fractionated. The fraction with b.p. 80–97°C/3 mm Hg contained 0.7 g (4 mmol, 9%) of S,S-diethylmethyldithiophosphonate (^{31}P-NMR: 78 ppm) and 2.2 g (12 mmol, 26%) of O-(methylchloroformoimino)chloromethylphosphonate (^{31}P-NMR: 42.6 ppm) (identified in comparison with an authentic sample). The fraction with b.p. 102–112°C/3 mm Hg contained 0.2 g (1 mmol, 2%) of S-ethyl-O-(methylchloroformoimino)methylphosphonate **5** (^{31}P-NMR: 61.9 ppm, identified in comparison with an authentic sample). The fraction with b.p. 120–140°C/3 mm Hg solidified when kept in the cold and was identified as bis(O-methylchloroformoimino)methylphosphonate **4**(1.2 g, 5 mmol, 11%). ^{31}P-NMR: 38.5 ppm. ^{1}H-NMR, δ: 1.84d 3H J17; 2.4s 6H. IR-spectrum, ν, cm^{-1}: 1590 (C=N).

Preparation (6) of bis(O-methylchloroformoimino)methylphosphonate **4**: The mixture of O-(methylchloroformoimino)chloromethylphosphonate (4.3 g, 23 mmol) and O-(trimethylsilyl)-methylchloroformooxime (3.5 g, 21 mmol) in toluene (15 ml) was heated at 140°C for 16 hours in a closed vessel. Volatile products were removed under vacuum and the residue was distilled to give bis(O-methylchloroformoimino)methylphosphonate **4** (4.2 g, 17 mmol, 76%) with b.p. 113°C/0.05 mm Hg, m.p. 68°C. ^{31}P-NMR: 38.5 ppm. ^{1}H-NMR, δ: 1.84d 3H J17; 2.4s 6H. IR-spectrum, ν, cm^{-1}: 1590 (C=N). Anal.: Calcd. for $C_5H_9Cl_2N_2O_3P$: C 24.31; H 3.67; N 11.34. Found: C 24.42; H 3.80; N 11.15.

Interaction of O-(methylchloroformoimino)trichloromethylphosphorane with 2-mercaptoethanol (**7**): A solution of O-(methylchloroformoimino)trichloromethylphosphorane (85 mmol) in ether (325 ml) was stirred at −35°C while a solution of 2-mercaptoethanol (7.0 g, 90 mmol) in ether (75 ml) was added. The mixture was allowed to warm to room temperature until the slurry disappeared. Ether was removed and the residue distilled to give 5.0 g (20 mmol, 24%) of O-[methyl-S-(β-chloroethyl)formoimino]chloromethylphosphonate **6** with b.p. 76°C/0.02 mm Hg, n_d^{20} 1.5085. ^{31}P-NMR: 43.1 ppm. ^{1}H-NMR, δ: 2.1d 3H J16; 2.47s 3H; 3.03t 2H J8; 3.76t 2H J8. Anal.: Calcd. for $C_5H_{10}Cl_2NO_2PS$: C 24.01; H 4.03; N 5.6. Found: C 23.51; H 3.82; N 5.15.

Preparation (8) of N,N-diethylamido-O-[methyl-S-(β-chloroethyl)formoimino]methylphosphonate **8**: To a solution of O-[methyl-S-(β-chloroethyl)formoimino]chloromethylphosphonate **6** (2.1 g, 8 mmol) in benzene (20 ml) a solution of diethyl amine (1.3 g, 18 mmol) in benzene (5 ml) was added. The reaction mixture was heated 0.5 hour at 100°C, cooled and filtrated. On distillation N,N-diethylamido-O-[methyl-S-(β-chloroethyl)formoimino]methylphosphonate **8** (0.35 g, 1 mmol, 15%) with b.p. 105–107°C/0.02 mm Hg, n_d^{20} 1.4893 was obtained. ^{31}P-NMR: 35.9 ppm. ^{1}H-NMR, δ: 1.11t 6H J8; 1.5d 3H J16; 2.36s 3H; 3.06m 6H; 3.75t 2H J8. Anal.: Calcd. for $C_9H_{20}ClN_2O_2PS$: C 37.70; H 7.03; N 9.77. Found: C 37.20; H 7.08; N 10.04.

Downloaded At: 14:44 29 January 2011

Interaction of O-(methylchloroformoimino)trichloromethylphosphorane with mercaptoacetic acid (**10**): A solution of O-(methylchloroformoimino)trichloromethylphosphorane (85 mmol) in ether (250 ml) was stirred at −35°C while mercaptoacetic acid (8.3 g, 90 mmol) was added. The mixture was allowed to warm to room temperature and ether was removed. The residue was distilled to give O-(methylchloroformoimino)chloromethylphosphonate (2.5 g, 13 mmol, 15%). ^{31}P-NMR: 43.0 ppm. ^{1}H-NMR, δ: 2.11d 3H J18; 2.46 s 3H.

Interaction of O-(alkylchloroformoimino)trichloromethylphosphoranes with thioacetic acid (**11**):

Interaction resulting in O-(alkylchloroformoimino)chloromethylthionophosphonate **2** *formation, general procedure.* A solution of O-(alkylchloroformoimino)trichloromethylphosphorane (50 mmol) in toluene (35 ml) was stirred at −30°C while thioacetic acid (3.8 g, 50 mmol) was added. The mixture was allowed to warm to room temperature and toluene was removed under vacuum. Distillation of the residue gave the corresponding O-(alkylchloroformoimino)chloromethylthionophosphonate **2** (Tables I and II).

Interaction resulting in O-(methyl-S-acetylformoimino)chloromethylthionophosphonate **11** *formation.* A solution of O-(methylchloroformoimino)trichloromethylphosphorane (50 mmol) in toluene (75 ml) was stirred at −30°C while a solution of thioacetic acid (7.6 g, 100 mmol) in toluene (6 ml) was added. The mixture was allowed to warm to room temperature and toluene was removed under vacuum. Distillation of the residue gave O-(methyl-S-acetylformoimino)chloromethylthionophosphonate **11** (3.9 g, 16 mmol, 32%) with b.p. 45°C/0.02 mm Hg, n_d^{20} 1.5398. ^{31}P-NMR: 97.2 ppm. ^{1}H-NMR, δ: 2.39d 3H J15; 2.46s 3H; 2.49s 3H. IR spectrum, ν, cm^{-1}: 780 (P=S); 1600 (C=N); 1720 (C=O). Anal.: Calcd. for $C_5H_9ClNO_2PS_2$: C 24.44; H 3.69; N 5.70. Found: C 23.95; H 4.10; N 5.80.

Preparation (12) of O-amyl-O-(ethylchloroformoimino)methylthionophosphonate **12**: To a solution of O-(ethylchloroformoimino)chloromethylthionophosphonate **2** (4.1 g, 19 mmol) in toluene (25 ml) a solution of potassium amylate (2.3 g, 18 mmol) in amyl alcohol (5.2 g, 59 mmol) was added under cooling. The mixture was boiled 1.5 hour at 100°C and then allowed to cool. After washing with water (3 × 20 ml) and drying with magnesium sulphate the solvent was removed under vacuum. The residue was distilled to give 1.1 g (4 mmol, 21%) of O-amyl-O-(ethylchloroformoimino)methylthionophosphonate **12** with b.p. 97°C/0.05 mm Hg, n_d^{20} 1.4854. ^{31}P-NMR: 99.2 ppm. ^{1}H-NMR, δ: 0.94t 3H; 1.3t 3H J8; 1.37m 4H; 1.66m 2H; 1.91d 3H J15; 2.64m 2H J8; 4.07m 2H. Anal.: Calcd. for $C_9H_{19}ClNO_2PS$: C 39.78; H 7.05; N 5.15. Found: C 40.15; H 6.87; N 4.65.

Preparation (12) of O-ethyl-O-(ethylchloroformoimino)methylthionophosphonate **12**: To a solution of O-(ethylchloroformoimino)chloromethylthinophosphonate **2** (5.0 g, 23 mmol) in toluene (30 ml) a mixture of ethanol (2.4 g, 52 mmol) and pyridine (4 g, 50 mmol) was added. The reaction mixture was boiled 6 hour at 100°C and then allowed to cool. After washing with water (3 × 15 ml) and drying with magnesium sulphate the solvent was removed under vacuum. The residue was distilled to give 1.0 g (4.5 mmol, 19%) of O-ethyl-O-(ethylchloroformoimino)methylthionophosphonate **12** with b.p. 81°C/3 mm Hg, n_d^{20} 1.4973. ^{31}P-NMR: 99.1 ppm. ^{1}H-NMR, δ: 1.3t 3H J6; 1.33t 3H J6; 1.9d 3H J16; 2.64m 2H J8; 4.17m 2H. Anal.: Calcd. for $C_6H_{13}ClNO_2PS$: C 31.38; H 5.70; N 6.10. Found: C 31.75; H 5.72; N 6.45.

ACKNOWLEDGEMENT

The authors thank Dr. A. N. Pushin and Prof. I. V. Martynov for many stimulating discussions.

REFERENCES

1. Yu. E. Lyashenko, V. B. Sokolov and I. V. Martynov, *Phosphorus, Sulfur, and Silicon*, **60**, 85 (1991).
2. K. V. Karavanov and S. Z. Ivin, *Zh. Obsh. Khim.*, **35**, 78 (1965).
3. K. V. Karavanov, L. E. Dmitrieva and S. Z. Ivin, *Zh. Obsh. Khim.*, **38**, 1547 (1968).
4. M. J. Dagani, U.S. Pat. 3,624,159; C. A., **76**, 46304z (1972).
5. B. V. Timochin, *Uspekhi Khim.*, **54**, 2027 (1985).
6. I. V. Martynov, A. N. Ivanov, T. A. Epishina and V. B. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **9**, 2128 (1988).

Downloaded At: 14:44 29 January 2011

7. V. B. Sokolov, A. N. Ivanov, T. A. Epishina and I. V. Martynov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **2**, 464 (1990).
8. B. Miller, *Proc. Chem. Soc.*, 303 (1962).
9. M. V. Vovk, A. A. Esipenko, V. N. Fetuchin, V. I. Boiko and L. I. Samarai, *Ukr. Khim. Zhur.*, **57**, 202 (1991).
10. G. Bauer and G. Hägele, *Angew. Chem. Intern. Ed. Engl.*, **16**, 477 (1977).
11. E. M. Meade and F. N. Woodward, *J. Chem. Soc.*, 1894 (1948).

Downloaded At: 14:44 29 January 2011